

**CONCISE ENCYCLOPEDIA  
OF POLYMER SCIENCE  
AND ENGINEERING**

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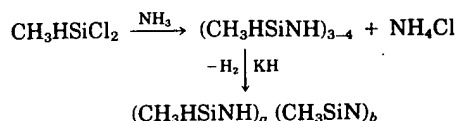
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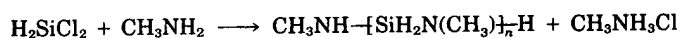
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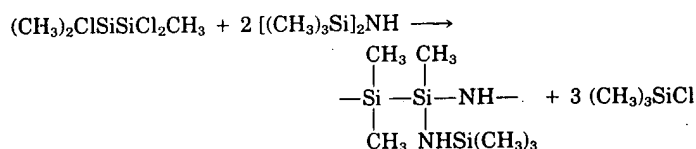


**Aminolysis of  $\text{H}_2\text{SiCl}_2$ .** Methylamine and dichlorosilane give *N*-methylpolysilazanes.



About 70% of the polymer consists of linear silazanes with  $\text{CH}_3\text{NH}$  endblocks and a number-average molecular weight  $M_n$  of 570.

**Silazanolysis of Methylchlorosilanes.** Heating methylchlorosilanes with hexamethyldisilazane gives methylpolydisilazanes through Si—Cl/Si—N redistribution:



**Chemical Vapor Pyrolysis.** Silicon nitride precursors can be prepared from  $[(\text{CH}_3)_2\text{SiNH}]_n$  and its isomer  $(\text{CH}_3\text{HSiNCH}_3)_n$ . Polymers are prepared from these cyclic compounds by catalytic reequilibration at 225–300°C. Complete conversion to ceramics occurs after heating to 700°C.

**Plasma Pyrolysis.** A glow-discharge polymerization has been described of hexamethyldisilazane in a mixture of gases consisting of ammonia, argon, nitrogen, and hydrogen.

### Silicon–Carbon–Oxygen Ceramic Systems

**Hydrolysis of Trialkoxysilanes.** Sol–gel routes to ceramics are currently the subject of extensive research. This technology involves the hydrolysis of metal alkoxides (usually with the formation of inorganic aquasols), followed by gelation and ultimately thermolysis of the gels. Films, fiber, and monolithic articles have been prepared by this route. The advantage to ceramic technology is the lower temperature required to convert the precursor to dense ceramics. This allows applications and compositions that do not tolerate higher temperatures, such as ceramic fibers or electronic devices.

**Hydrolysis of  $\text{RSi}(\text{OR}')_3$  with Inorganic Sols.** Methylsilsesquioxanes containing silica or alumina were prepared by hydrolysis of methyltrimethoxysilane in alumina or silica aquasols.

### Other Precursors

The search for suitable low temperature polymer synthesis and fabrication routes to high technology ceramics of boron, aluminum, and a few transition metals is showing some promise.

Boron-containing systems include borosiloxane polymers, carborane–siloxane polymers, and boron–nitrogen polymers.

Aluminum-containing systems include organometallic aluminum precursors.

**Systems Containing Transition Metals.** Low temperature pyrolysis of organometallic complexes could provide an inexpensive fabrication method for stoichiometric transition-metal ceramics for electronic, structural, or refractory applications.

Though there are significant challenges to this technology,

opportunities to use polymer processing for ceramics are only beginning to be tapped. Japanese researchers described the use of preceramic polymers to produce sinterable powders. Preceramic polymers may be used for ceramic coatings or as binders. Ceramic foams may supply high temperature insulating materials. Polymer forms such as fibers, foams, films, binders, and adhesives are well known to the polymer chemist, but are only now beginning to be utilized by ceramists through preceramic polymer technology.

### BIBLIOGRAPHY

- K. J. Wynne and R. W. Rice, *Ann. Rev. Mater. Sci.* **14**, 297 (1984).  
 S. Yajima, J. Hayashi, M. Omori, and K. Okamura, *Nature* **261**, 683 (1976).  
 R. H. Baney, *Chem. Tech.* **17**, 738 (1988).

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**PRECIPITATION POLYMERIZATION.** See ACRYLONITRILE POLYMERS; RADICAL POLYMERIZATION; SOLUTION POLYMERIZATION.

**PREFORMS.** See REINFORCED PLASTICS.

**PREIMPREGNATED MATERIALS.** See REINFORCED PLASTICS.

**PREPEGS.** See REINFORCED PLASTICS.

### PREPOLYMER

A prepolymer is a partially polymerized substance, or one polymerized to a low degree of polymerization, for subsequent conversion to a high polymer (see also POLYMER).

**PRESERVATIVES.** See BIOCIDES.

**PRESSURE BAG MOLDING.** See REINFORCED PLASTICS.

### PRESSURE-SENSITIVE ADHESIVES AND PRODUCTS

Pressure-sensitive adhesives (PSAs) are used mainly for adhesive tapes and labels. Lesser but nonetheless important applications are for medical products, protective masking sheets, and specialty products.

The term pressure-sensitive designates adhesives "which in dry form are aggressively and permanently tacky at room temperature and firmly adhere to a variety of dissimilar surfaces

upon mere contact without the need of more than finger or hand pressure". Unlike early materials such as pitches and gums, and unlike self-bonding cements or even sticky substances like fly paper, a PSA requires no activation by solvents or heat and exerts a strong adhesive force toward a variety of surfaces, including paper, glass, wood, metals, plastics, skin, and others. Moreover, according to the Pressure Sensitive Tape Council (PSTC) "they have a sufficiently cohesive holding and elastic nature so that, despite their aggressive tackiness, they can be handled with the fingers and removed from smooth surfaces without leaving a residue".

### Construction and Components

Pressure-sensitive products consist of a flexible backing coated with an adhesive; many require a release liner or coating for ease of delivery and application. By definition, the release surface confers low adhesion to the PSA. A typical construction of a PSA tape is shown in Figure 1. Label construction is similar, but always includes a release liner. The distinction between labels and decals is not clear, although the latter connotes display or advertising.

In the manufacture of tapes, the adhesive is coated on a continuously moving web. Frequently, the adhesive is coated on a release liner, paper, or film with an adherent coating, which is then laminated, using pressure applied by roller nips, to a backing to which it has high adhesion. For the manufacture of labels and many medical products, the release liner is never removed but becomes an integral part of the final package, whether in roll or sheet form. The adhesive usually is applied directly to the backing of tapes.

Adhesives are supplied to the coating operations as solutions in organic solvents, aqueous emulsions, or 100% solids. An emerging technology, not yet of industrial importance, is radiation polymerization of adhesive components on a moving web. Radiation cross-linking of preformed polymers is of minor importance.

**Backings.** The choice of backing material is governed by the PSA application.

The most widely used backing in both tapes and labels is paper. It constitutes perhaps 80% of the backing market for labels. Second in volume is oriented polypropylene, used mainly for carton and box sealing. Other widely used backings are glass filament-reinforced films and papers, polyethylene-coated cloth, acetate film (which is now the principal backing for the ubiquitous cellophane tape), poly(ethylene terephthalate), poly(vinyl chloride), and aluminum foil. Specialty backings in flexible-film form include foams, fabric-reinforced epoxies, nylons, polyurethanes, and polyethylene.

**Release Coatings.** Release coatings are of great importance for pressure-sensitive products. Tapes in roll form usually carry release coatings on their reverse sides or a release-coated interliner. The release treatment on self-wound tapes may use silicones, alkyds, stearyl derivatives of vinyl polymers, stear-

ate chromic chloride, or agents like stearamides. All labels and some specialty products (ostomy devices, medical devices, etc), and double-faced tapes require a release-coated sheet to permit delivery. Release liners, which are based on paper or films, are almost always silicone-coated.

**Tackifiers.** All rubber-based adhesives require resin tackifiers as a main component. These materials impart tack or stickiness. The tackifier content of rubber-based adhesives is usually 60–110 pph elastomer. Acrylic PSAs utilize tackifiers in smaller amounts.

By far the largest volume tackifiers are the hydrocarbon resins obtained by oligomerization of the  $C_5$  and  $C_9$  fractions of petroleum. The  $C_5$  fraction tackifiers, including hydrogenated fractions, are most compatible with PSA base polymers.

Other tackifiers of significance are rosin esters, coumarone-indene resins and copolymers of  $\alpha$ -methylstyrene and vinyltoluene, which resemble the  $C_9$  hydrocarbon tackifiers (see HYDROCARBON RESINS).

### Raw Materials

**Natural Rubber.** Natural rubber (NR), derived from the latex of the *Hevea brasiliensis* tree, is all *cis*-1,4-polyisoprene (see RUBBER, NATURAL). Blending NR with tackifiers produces high quality PSAs, the properties of which are determined by the tackifier. A mixture of tackifiers often gives better results than a single resin. Fillers, such as clays, modify properties and reduce costs. Antioxidants are included to protect the unsaturated backbone polymer from degradation. Plasticizers, such as petroleum oils or low molecular weight polyisobutylene, are added to many formulations.

**Block Copolymers.** Triblock copolymers of the form A-B-A, where A is polystyrene (S) and B is a polydiene, have recently surpassed NR as the most widely used hydrocarbon rubber in PSAs. These polymers are trademarked as Kraton by Shell, the only domestic producer. S-I-S triblock copolymers behave as thermoplastic elastomers with a low melt viscosity; they are well suited for hot-melt adhesives. These characteristics permitted development of 100%-solids PSA formulations. At present, hot-melt PSAs, which make up about 20% of the market, are almost entirely based on these block copolymers.

A significant portion of block copolymer is used in solution adhesives, primarily for paper-backed tapes.

Typical styrene-isoprene-styrene block copolymer PSA formulations are given in Table 1. (Note that end-block tackifiers are sometimes omitted.)

**Styrene-Butadiene Rubber.** The styrene-butadiene random copolymer used for adhesives differs from the typical elastomer SBR. Because of the higher polymerization temperature (50–60°C), the PSA has a broader molecular weight distribution and often a gel fraction, both of which are desirable.

Solution adhesives using gum SBR are more widely used than SBR latex.

**Polyisobutylene.** The polymerization of isobutylene yields polyisobutylene (PIB) in a broad range of molecular weights. The vulcanizable elastomer polymerized with 0.8–2% isoprene is called butyl rubber. In many applications, PIB and butyl rubber are interchangeable (see ISOBUTYLENE POLYMERS).

Butyl rubber is used in pipe-wrap adhesives, which are calendered onto PVC or polyethylene backings. A wide variety of tackifiers are used with butyl. The principal application of PIB adhesives, usually as solutions in petroleum fractions (naph-

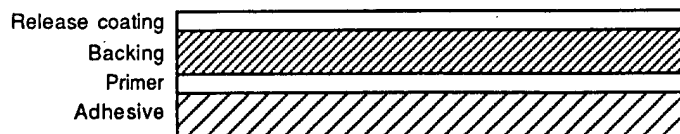


Figure 1. Laminated construction of pressure-sensitive tape.